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PCB REMOVAL - SOLVENT EXTRACTION

Report No 82-371-K
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ABSTRACT

PCB was removed from contaminated insulating oil using methanol or acetonitrile as the extraction solvent in a packed column liquid/liquid extractor. About 50-70% by volume of oil was recovered which contained approximately 10% by weight of the original PCB. The remaining oil must be treated as concentrated PCB waste. Acetonitrile performed better than methanol and calculations indicate a three-stage extractor system using acetonitrile as solvent could produce 93% by volume of PCB-free product for input oils contaminated with up to 300 mg/kg PCB. Solvent extraction of PCB's from large volumes of insulating oils is not considered competitive with recently developed alkali metal dechlorination processes.

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To Mr. B.K. Smith
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PCB REMOVAL - SOLVENT EXTRACTION

Under present Ministry of the Environment guidelines, insulating oil containing more than 25 mg/kg polychlorinated biphenyls (PCB) is considered a potential environmental hazard and its storage or disposal must meet stringent regulations/1/. There is thus a need for a process which could remove PCB from contaminated oil and free large quantities of oil for electrical use or conventional waste disposal. This report evaluates solvent extraction as a method of PCB removal from contaminated insulating oil.

Solvent Selection

A solvent suitable for the removal of PCB from oil should have the following characteristics:

(1) A high affinity for PCB and low affinity for oil.

(2) A density significantly different from that of insulating oil to aid post-contact separation.

(3) A boiling point much lower than that of the PCB homologues to permit their removal from the solvent by simple distillation.

The solvents furfural, aniline, phenol (90%), glacial acetic acid, acetonitrile, methanol, and ethylene glycol were identified in a previous report/2/ as those most likely to meet the above requirements and all demonstrated acceptable affinity for PCB in oil/solvent contact tests. Of these methanol, acetonitrile and glacial acetic acid were selected for testing in a PCB extraction system because of the low relative volatility of PCB at boiling solvent temperatures and the reduced energy requirements for distillation. In addition, the high boiling point solvents phenol, furfural and aniline are considered highly toxic by skin absorption and inhalation/3,4/, and pose significant operating hazards.

Test Method

Extraction tests were performed in a modified Soxhlet extractor. The solvent is cycled in a closed loop between a solvent still and an extraction reservoir as follows:

(1) Vapour output of a solvent still is directed to the top of an extraction reservoir where it is condensed.

(2) The condensed solvent contacts PCB-contaminated insulating oil by gravity flow through a packed column.

(3) The PCB-laden solvent separates as a phase distinct from the oil and flows by gravity to the solvent still.

The apparatus and method are described in Appendix 1.

Results

PCB extraction using methanol and acetonitrile proceeded smoothly but with either solvent a steady loss of insulating oil from the extraction reservoir was observed. The solvent returning to the still was clear indicating that oil carryover was a result of dissolved oil and not suspended droplets.

Extreme oil carryover caused by turbulent solvent flow from the extractor was observed in the glacial acetic acid tests. Despite system changes, the transfer of suspended and dissolved oil to the solvent still could not be prevented and continuous extraction tests with this solvent were discontinued in favour of batch processing.

The batch approach eliminated suspended oil droplet carryover in the acetic acid as sufficient time was allowed for a distinct phase separation to occur. However, dissolved oil carryover was 2.5 times that with methanol under similar conditions and work with this solvent was discontinued.

PCB extraction results for the solvents methanol and acetonitrile are given in Appendix 2 and are described below.

In test 1, using methanol, and test 2, using acetonitrile, the extraction continued until 50% of the input oil volume had accumulated in the solvent still as a result of carryover. For oil with an initial PCB content of 180 mg/kg, methanol extracted 89% and acetonitrile 97% of the PCB under otherwise identical conditions.

The PCB contents of the extracted oils were less than the 25 mg/kg target level but were higher than the <2 mg/kg level expected based on the partition coefficient data of Reference 2. This indicates that equilibrium conditions are not reached in the continuous-flow, packed-column extractor, probably because of backmixing of PCB extracted oil and PCB contaminated feed during extraction, a typical problem of simple column extractors/5,6/.

Tests 1, 3 and 4, where methanol was used to extract PCB from oils contaminated with 180, 500 and 1000 mg/kg PCB, showed PCB reductions of 89, 95 and 87%, respectively, under otherwise identical conditions. These results indicate the absence of a

significant concentration effect over the range of PCB concentrations: 0 to 1000 mg/kg, when methanol is the solvent.

When acetonitrile was used in tests 2, 5 and 6 to extract oils contaminated with 500, 850 and 2500 mg/kg PCB, PCB reductions of 96, 89 and 91%, respectively, were observed and a significant concentration effect over the test range of PCB concentration was not identified. The oil carryover in these tests was held to 33% as at this level the extraction performance was comparable to that of methanol in tests 1, 3 and 4.

In all tests the extractor/still system partitioned the oil into two fractions, a low PCB content fraction possibly suitable for use in electrical equipment, and a high PCB content fraction having a PCB content higher than that of the input oil.

The large waste volumes produced with either methanol or acetonitrile rule out use of these solvents in a single column extractor system for PCB removal from contaminated insulating oil at expected PCB contents of a few hundred milligrams per kilogram. However, a series of extractors in which the high PCB content output of one extractor is treated as input by the next extractor in the series is considered a potentially effective method of waste product volume reduction if PCB extraction efficiency can be maintained over the PCB concentration range expected.

An extractor cascade using three extractors is shown schematically in Figure 3 of Appendix 3. Table I of Appendix 3 gives the calculated product volumes and PCB contents expected, assuming the extraction efficiency and carryover oil volumes at each stage remain approximately the same as those found in tests 1 to 6.

Calculations and flow diagrams showing steady-state extractor conditions are also given in Appendix 3.

For acetonitrile the three-stage cascade is potentially successful for PCB contents $\leq$300 mg/kg but 7% waste product is expected for each batch of oil processed. For methanol more than three stages would be required to achieve comparable results and this discourages the use of methanol as an extraction solvent.

The efficiency of the extractor can probably be increased, especially in stages 2 and 3, by using a mixer/settler contactor design instead of the simple packed column. Such a system will eliminate backmixing of PCB-saturated solvent and PCB-depleted oil/5,6/. However, the increased complexity and space requirements of a mixer/settler system are considered excessive for the task at hand as at least one PCB destruction method, using an alkali metal as reagent, has been successfully demonstrated/8,9/. In addition, the extraction method can, at best, concentrate PCB waste and thus only reduce the volume of stored material.

Conclusions

(1) Solvent extraction using methanol or acetonitrile as solvent can remove PCB from contaminated insulating oil but the PCB concentrate produced contains a significant volume of oil.

(2) Packed column extractors of the form described in Appendix 1 permit excessive backmixing between PCB saturated solvent and the extracted oil and are not suitable for solvent extraction using methanol or acetonitrile.

(3) Replacement of the packed column with a series of mixer/settler contactors could enhance PCB extraction but tests at this time are not warranted as superior PCB destruction technologies have been successfully demonstrated on a large scale.

Recommendation

Work on solvent extraction for the removal of PCB from insulating oil should be discontinued in favour of chemical destruction methods employing alkali metals.

Approved:

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APPENDIX 1

APPARATUS AND METHOD

(a) Apparatus

A standard Soxhlet extraction system is shown schematically in Figure 1. The modified extractor sections used for liquid/liquid contacting and which replace the usual porous cup are shown in Figure 2. The following are noted:

(1) The o.d. of the solvent collector funnel (Figure 2) approximately equals the id of the Soxhlet extraction chamber (Figure 1) so that minimal condensing solvent can bypass the oil reservoir.

(2) Column packing in the form of star-shaped teflon disks (Figure 2) is provided to break the input solvent into droplets and compartmentalize the extractor to minimize backmixing.

(3) Solvent discharge from the extraction chamber is by siphoning, initiated when the solvent level reaches the overflow level shown in Figure 1. The siphoning action causes a temporary rise in the rate of solvent vapour production and, therefore, condensation so that solvent flow through the extractor is pulsed as well as continuous.

The above simulates a pulsed, packed extraction column, a device common in industrial extraction processes/5,6,7/.

(b) Method

The extractions proceed as follows:

(1) 20 to 40 g of PCB-contaminated oil are placed in the extraction reservoir and the still is charged with 160 mL solvent.

(2) Solvent flow is controlled by the heating rate of the still heater and is adjusted during tests to provide an average flow rate of 0.2 mL/g oil/min. The still temperature is maintained approximately at the normal boiling point of the solvent used, ie, 65°C for methanol, 82°C for acetonitrile and 118°C for glacial acetic acid.

(3) Extraction stops when a predetermined percentage of input oil has passed to the still depending on the solubility of oil in the solvent. Thirty to sixty per cent carryover was required to effect reasonable PCB stripping from the input oil sample.

(4) Waste oil collected in the still is separated from the solvent by a combination of solvent distillation and gravity separation at 25°C.

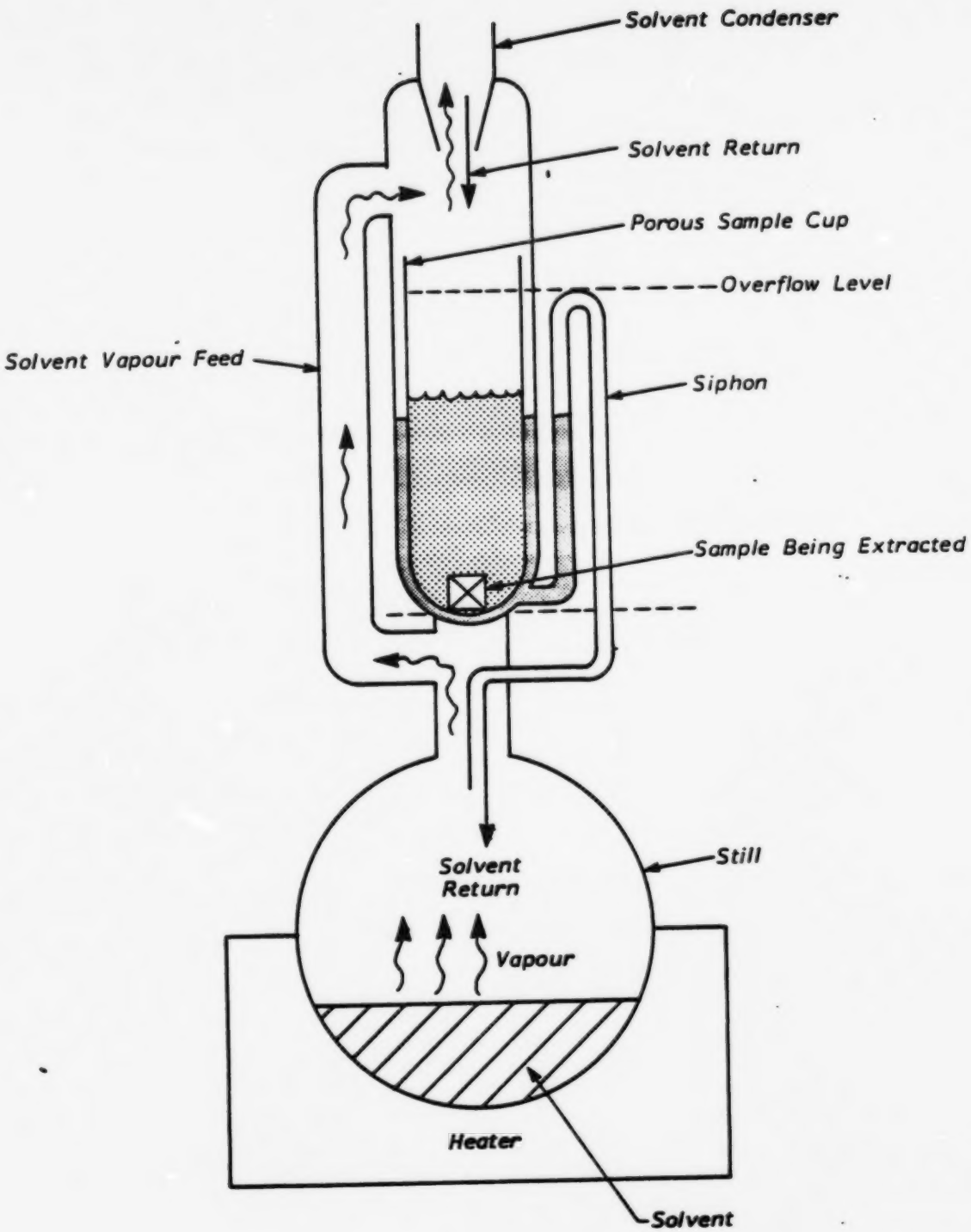


FIGURE 1

STANDARD SOXHLET EXTRACTOR-SCHEMATIC (AS USED TO EXTRACT SOLIDS)

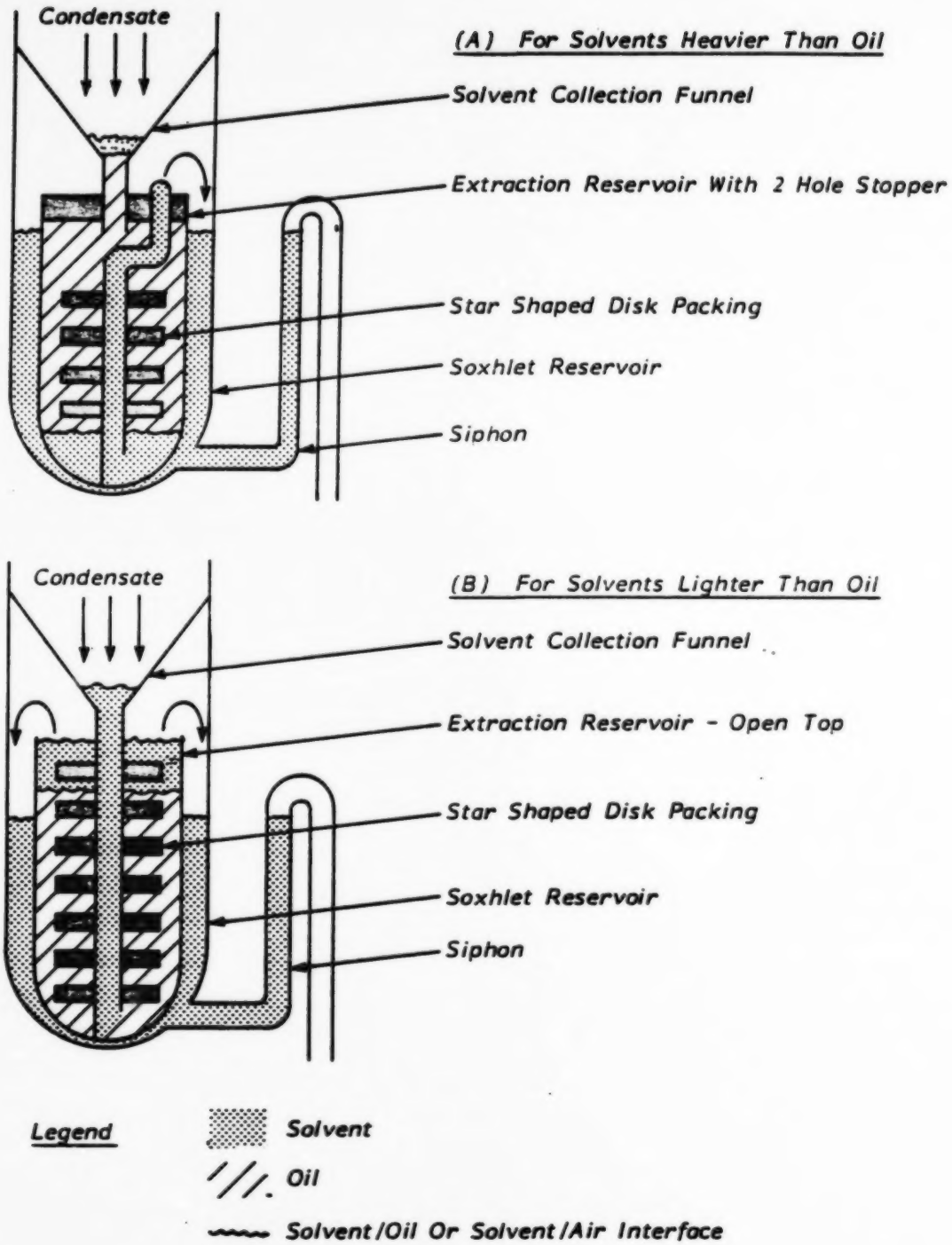


FIGURE 2

EXTRACTOR SECTIONS FOR USE WITH SOXHLET EXTRACTOR - (REPLACE POROUS CUP OF FIGURE 1)

APPENDIX 2

EXTRACTION TEST RESULTS*

Test Number	Solvent	PCB Content (mg/kg)			Oil Mass (g)		Test Duration (min)
		Initial Oil	Final Oil	Waste Oil	Initial Oil	Final Oil	
1	Methanol	180	20	340	30	15	255
2	Acetonitrile	180	5	360	30	15	255
3	Methanol	500	25	980	30	15	255
4	Methanol	1000	130	2800	30	15	225
5	Acetonitrile	850	90	2400	30	20	190
6	Acetonitrile	2500	230	7000	30	20	190

* Solvent flow rate = 0.2 mL solvent/g oil/min.
Extractor temperature = 30°C.
Still temperature = 65°C for methanol and 82°C for acetonitrile.

APPENDIX 3

EXTRACTOR CASCADE SYSTEM MODEL

(a) Feed and Product Volumes

Volumes of the various feeds and products can be calculated directly from the process flow diagram, Figure 3, by fixing the product volumes for the last extractor, then calculating other volumes, as encountered, by traversing the flow paths in the direction of the original feed.

(b) Feed and Product Concentrations of PCB

These may be calculated by enforcing a mass balance for PCB at each extractor but it is simpler to arrive at a solution numerically as follows:

(1) Set the expected feed concentration to extractor 1.

(2) Set the low PCB content outputs of extractors 2 and 3 arbitrarily at zero.

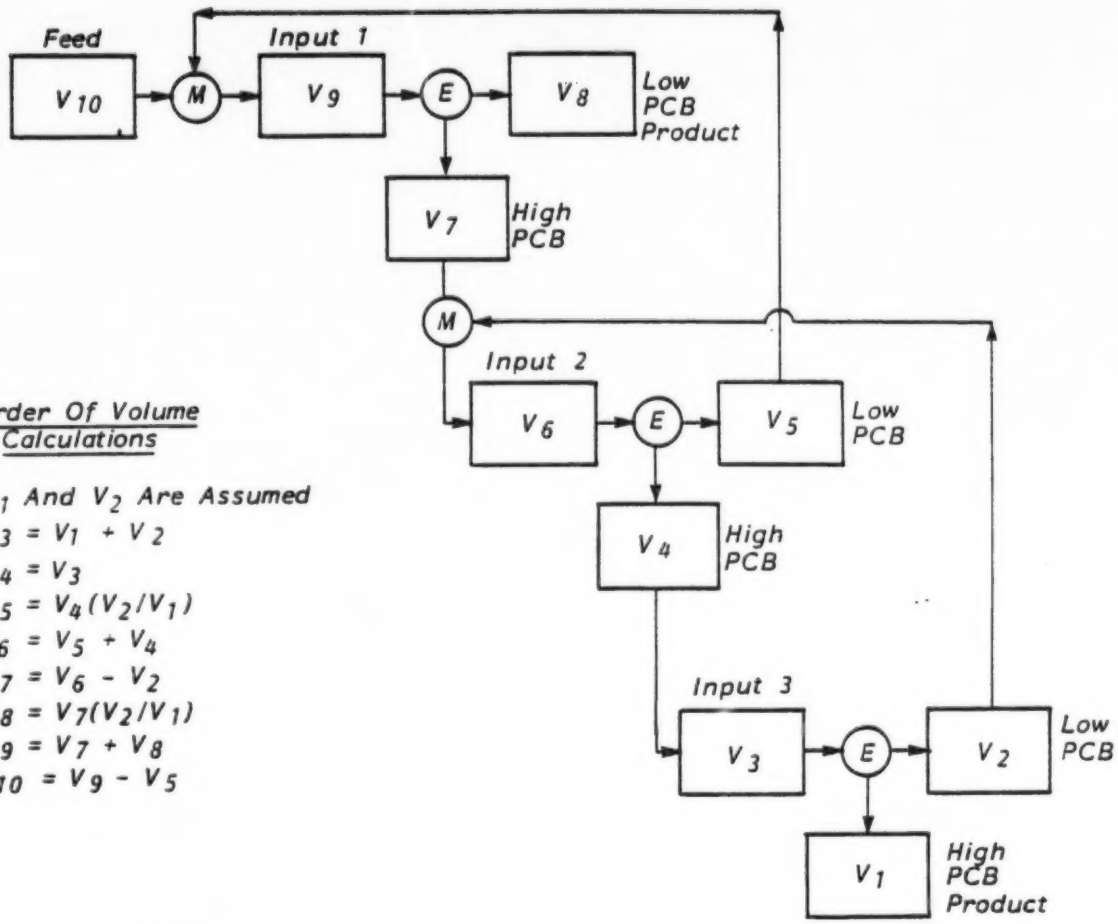
(3) Set the percentage PCB removal expected in the extractors based on experimental efficiencies. For example, Appendix 2 results for methanol show an 89% reduction in PCB concentration in one extractor, therefore, each extractor in the methanol cascade of Figure 4 is assumed to produce PCB reduced oil whose PCB concentration is 11% of the extractor's input PCB concentration.

(4) Calculate concentrations as encountered by traversing the flow paths from the original feed.

(5) Repeat step (4) until calculated concentrations do not change - usually four complete iterations.

Examples

(1) Figures 4 and 5 show the above process as applied to methanol and acetonitrile extractions of PCB-contaminated oil assuming constant separation efficiency and volume partitioning at each stage.



Order Of Volume Calculations

(1) V_1 And V_2 Are Assumed
(2) $V_3 = V_1 + V_2$
(3) $V_4 = V_3$
(4) $V_5 = V_4(V_2/V_1)$
(5) $V_6 = V_5 + V_4$
(6) $V_7 = V_6 - V_2$
(7) $V_8 = V_7(V_2/V_1)$
(8) $V_9 = V_7 + V_8$
(9) $V_{10} = V_9 - V_5$

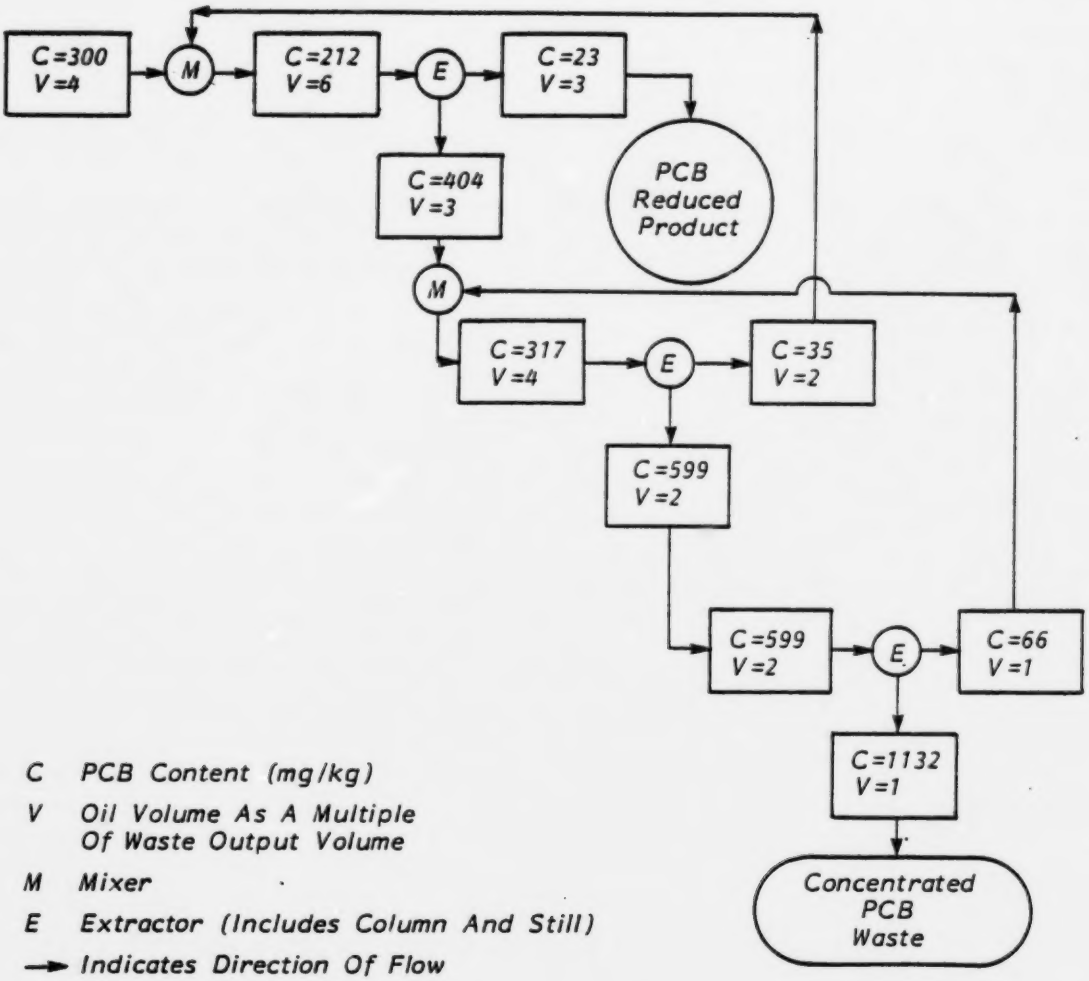
Legend

M = Mixer

E = Extractor (Includes Column And Still)

V = Input And Output Oil Volumes

FIGURE 3
3 STAGE EXTRACTION SYSTEM



C PCB Content (mg/kg)

V Oil Volume As A Multiple Of Waste Output Volume

M Mixer

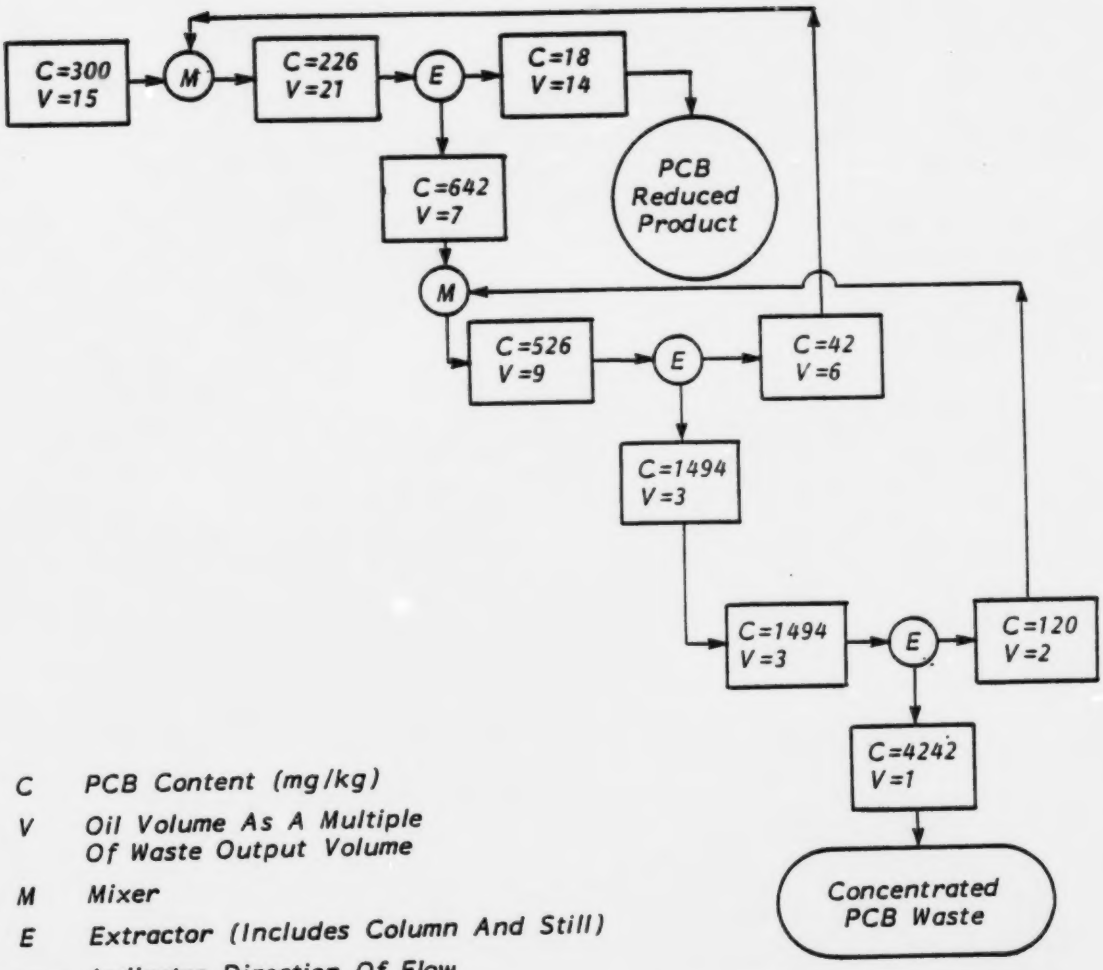
E Extractor (Includes Column And Still)

→ Indicates Direction Of Flow

* 1/1 Partitioning Of Input And 89% Extraction Efficiency Was Assumed At Each Extractor Stage. Waste Product Volume = 25% Of Input.

FIGURE 4

CALCULATED FLOW DIAGRAMS FOR A 3 STAGE METHANOL CASCADE*



C PCB Content (mg/kg)

V Oil Volume As A Multiple Of Waste Output Volume

M Mixer

E Extractor (Includes Column And Still)

→ Indicates Direction Of Flow

* 2/1 Partitioning In Favor Of PCB Reduced Product And 92% Extraction Efficiency Was Assumed At Each Extraction Stage. Waste Product Volume = 6.67% Of Input.

FIGURE 5

CALCULATED FLOW DIAGRAMS FOR A 3 STAGE ACETONITRILE CASCADE*

TABLE I

CALCULATED PRODUCT VOLUMES AND PCB CONCENTRATIONS
- THREE EXTRACTOR CASCADE

Solvent	Extraction Efficiency* (%)	Carryover Per Stage** (%)	PCB Contents			Oil Volumes - as % of Input	
			Input (mg/kg)	Output 1 (mg/kg)	Output 2 (mg/kg)	Output 1	Output 2
Methanol	89	50	300	25	1130	75	25
Acetonitrile	92	33	300	20	4240	93	7

* Per cent PCB reduction in one extraction stage. Average of tests 1, 3, 4 for methanol and tests 2, 5, and 6 for acetonitrile.

** Per cent of input oil volume carried to still during extraction.